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Improvement of the Thallium Cuprate Thin Films Due to an Optimization of the Doping Holes Densities as Seen by XAS

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T_c optimization of as-synthesized Tl 2212 thin films can be obtained through post-annealing treatments at low temperatures (180 and 220°C). In this paper, the optimization process was controlled by ac magnetic susceptibility measurements for the T_c's and by polarized X-ray absorption spectroscopy measurements for the doping hole densities. The latter technique allows a direct insight into the hole density only in the (*a*, *b*) plane of the Tl 2212 structure. All the studied thin films are overdoped with respect to the optimum of 0.12 doping holes per copper defined previously. T_c increases up to 6 K were observed after post-annealing treatments under an argon atmosphere and were correlated with significant reduction of the doping hole density. In contrast to what has been observed on sintered samples, a post-annealing treatment at 220°C resulted in an insufficient doping hole density, below the optimum, probably resulting from the small sample thickness.

INTRODUCTION

Thallium cuprate thin films are known to be more difficult to synthesize than YBCO thin films primarily due to the numerous parameters which must be controlled during the deposition process and the high volatility of thallium oxide at high temperature. This volatility complicates any *in situ* deposition process as the substrate cannot be heated at a sufficient temperature for good crystallization (≥800°C) (1, 2). The film must therefore be deposited at low temperature and crystallized *ex situ* in a sealed quartz tube under high oxygen and thallium oxide partial pressures. The exact hole densities in the final product are thus difficult to control. Although one can expect the as-synthesized film to be overdoped, a direct determination of the hole densities is necessary since this parameter has been shown to have a decisive influence on the superconducting properties (3).

Cu L_3-edge X-ray absorption has yielded a wealth of qualitative and quantitative information about hole doping in superconducting oxides. The presence of an additional shoulder on the high energy side can be ascribed to the dipole transition $2p^63d^9L \rightarrow 2p^53d^{10}L$ (4–6). The main absorption line itself is ascribed to the dipole transition $2p^63d^9 + 2p^63d^{10}L \rightarrow 2p^53d^{10}$.

Measurements of hole concentration provide means to determine the optimum value of hole concentration in terms of critical temperature. As is now well known, the T_c depends highly on the hole concentration and tends to decrease when the hole density departs from a certain optimum value. For instance, in the $TlBa_2Ca_{1-x}Nd_xCu_2O_{7-\delta}$ ($0.2 \leq x \leq 1$) (5) or $Bi_{2-x}Pb_xSr_2Ca_{1-x}Y_xCu_2O_{8-\delta}$ ($0 \leq x \leq 1$) series (6), the decrease of T_c with increasing x is accompanied by a diminishing of the shoulder indicative of the $2p^63d^9L \rightarrow 2p^53d^{10}L$ transition and a decrease in hole density. Similarly in Tl(2201) and Tl(2212) ceramics, annealed at low temperature in a reducing atmosphere, the decrease of the hole densities as a function of annealing time has been correlated to a striking increase of T_c in the Tl(2201) samples and to an optimization of T_c in the Tl(2212) samples (7).

In this work, we will study the influence of low temperature argon atmosphere post-annealings on the critical temperature of thallium cuprate thin films on T_c's as seen by XAS at Cu L_3-edge. Hole density measurements, by thermoelectric power, have been carried out on bulk polycrystalline material (8). It appears that thin films are much more sensitive than bulk material to any thermal treatment owing to the very small quantities of material involved. Thus a comparison between bulk material and thin films

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TABLE 1

Low pressure (LP)	Medium pressure (MP)	High pressure (HP)
sealed quartz tube 1 bar dwell temperature 840°C duration: 10 min	sealed quartz tube 10 bar dwell temperature 870°C duration: 10 min	sealed quartz tube 70 bar dwell temperature 880°C duration: 15 h

is valuable. The Tl(2212) thin films used throughout have been carefully characterized for orientation by X-ray diffraction such that polarized XAS experiments could probe only the doping hole densities in the (a, b) plane of the layered structure, the main parameter governing T_c's in HTC superconductors.

EXPERIMENTAL

The films were prepared by an *ex situ* one-step method (3, 9, 10). As a first step, Tl–Ba–Ca–Cu–O films were deposited on [100] oriented $LaAlO_3$ by multitarget sputtering. The deposition process has already been described in a previous paper (3) and is summarized below:

—Four cathodes are placed in a sputtering chamber in which the substrate holder is rotated at a low rotation speed (10 RPM).

–Insulating targets ($Ba_{1,8}Ca_{0,2}CuO_3$, and Ca_2CuO_3) are R.F. biased (with self-dc voltage between 500 and 1000 V).

—Metallic targets (Tl, Cu) are dc biased.

—The gas pressure is maintained at 10^{-2} mbar for argon and 10^{-3} mbar for oxygen.

Because of the high volatility of Tl_2O oxide, the substrate was not heated. The films after deposition are insulating and amorphous.

After deposition, the amorphous films were annealed in order to crystallize the 2212 phase. Three types of annealing treatments were performed on these films (see Table 1):

—sealed tube under low oxygen pressure (1 bar),

—sealed tube under medium oxygen pressure (10 bar),

—under high oxygen pressure (70 bar).

During all the annealings, the films were wrapped in gold foil in the presence of 2212 bulk material in order to provide an excess of thallium oxide pressure near the film. For the medium pressure annealing, oxygen was provided by the reaction between BaO_2 and Tl_2O_3 which takes place in a crucible placed in the tube close to the gold foil.

Post-annealing treatments can be applied to the films in order to modify T_c. For that purpose, the films are heated under an argon flow up to a temperature ranging between 180 and 220°C during 5 to 15 min (3). In the following, the as-synthesized samples will be noted LP, MP, or HP depending on the annealing treatment (low, medium, and high pressure). The post-annealed samples will be noted by adding a number corresponding to the treatment. Magnetic measurements were performed on a LAKE Shore susceptometer with ac fields of 1 G or on a Quantum Design SQUID with dc fields of 1 G applied after a zero field cooling. A scanning electron microscope (SEM) fitted with a TRACOR analytical system was used to observe the surface of the film and also to determine the composition (EDS mode) of the film before and after annealing. A SEIFERT diffractometer was used to obtain an X-ray diffraction pattern in order to check for the purity of the film and its orientation.

All the XAS spectra at the L_3-edge of copper were recorded at room temperature. The experiments were performed at LURE (Orsay) using synchrotron radiation from the super-ACO ring operated at 800 MeV with a typical current of 250 mA. The $LaAlO_3$ substrates of the thin films ($10 \times 2 \times 0.5$ mm^3) were glued to an aluminum sample holder by silver paste. In order to make good electrical contacts between the thin film and the sample holder, small contacts also with silver paste were realized at the corners of the thin films. The X-rays were monochromatized by two beryl crystals ($10\bar{1}0$) and the absorption coefficient was measured in total yield mode (TEY) using either a detection of the electrons by a channeltron or by measuring the sample current. The energy scale was then positioned with respect to the $|3d^9\rangle$ peak of CuO at 931.2 eV. The experimental energy resolution was estimated to be better than 0.3 eV, whereas the reproducibility of the energy position of the spectral features was close to 0.05 eV. The width of the core hole has been measured to be 0.56 eV at the copper L_3-edge (11). The usual thickness of the probed upper layer of the samples is about 150 Å in the total electron yield mode and more than 1000 Å in fluorescence yield mode.

The normalization has been made on the continuum before the L_2 peak around 948 eV. But, in order to compare directly the $|3d^9L\rangle$ peak intensity on some figures, the top of the $|3d^9\rangle$ transitions has been set to a common value chosen arbitrarily. To obtain the relative intensities of the transitions, the spectra have been least squares fitted by two pseudo-Voigt's shape functions following a process described previously (5–7).

RESULTS AND DISCUSSION

1. Sample Characterization

In order to optimize the superconducting properties and especially the T_c's, various annealing and post-annealing treatments have been made. The parameter which is changed during the annealing treatment is the oxygen partial pressure (see Table 1). For each pressure, the temperature of the dwell is adjusted in order to get the crystalliza-

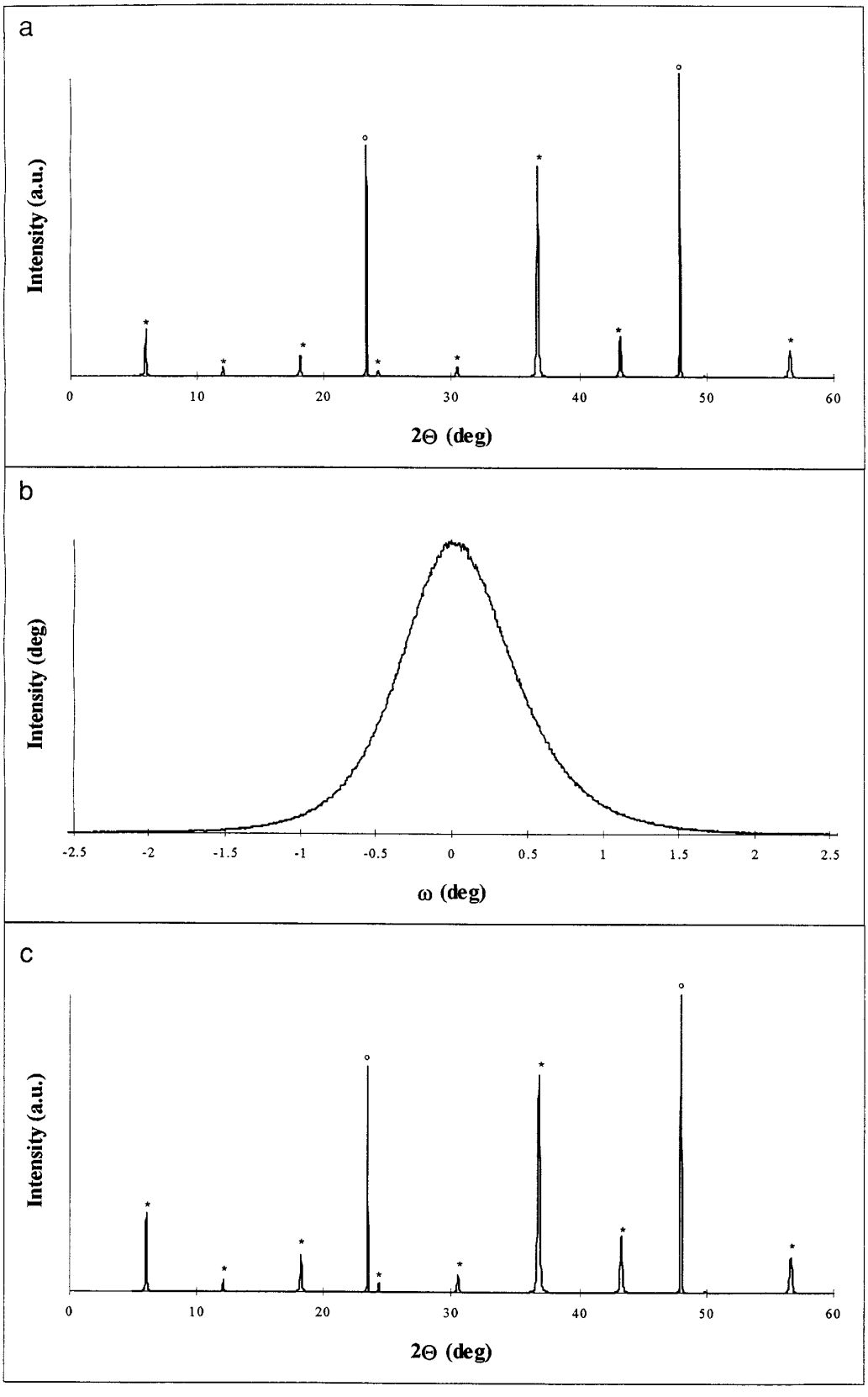

FIG. 1. X-ray diffraction patterns of Tl 2212 thin films (peaks marked o: substrate; peaks marked*: Tl2212 phase). (a) As-synthesized under 10 bar O_2. (b) Rocking curve for the same sample on the 0012 reflection. (c) As-synthesized under 10 bar O_2 post-annealed under Ar at 220°C.

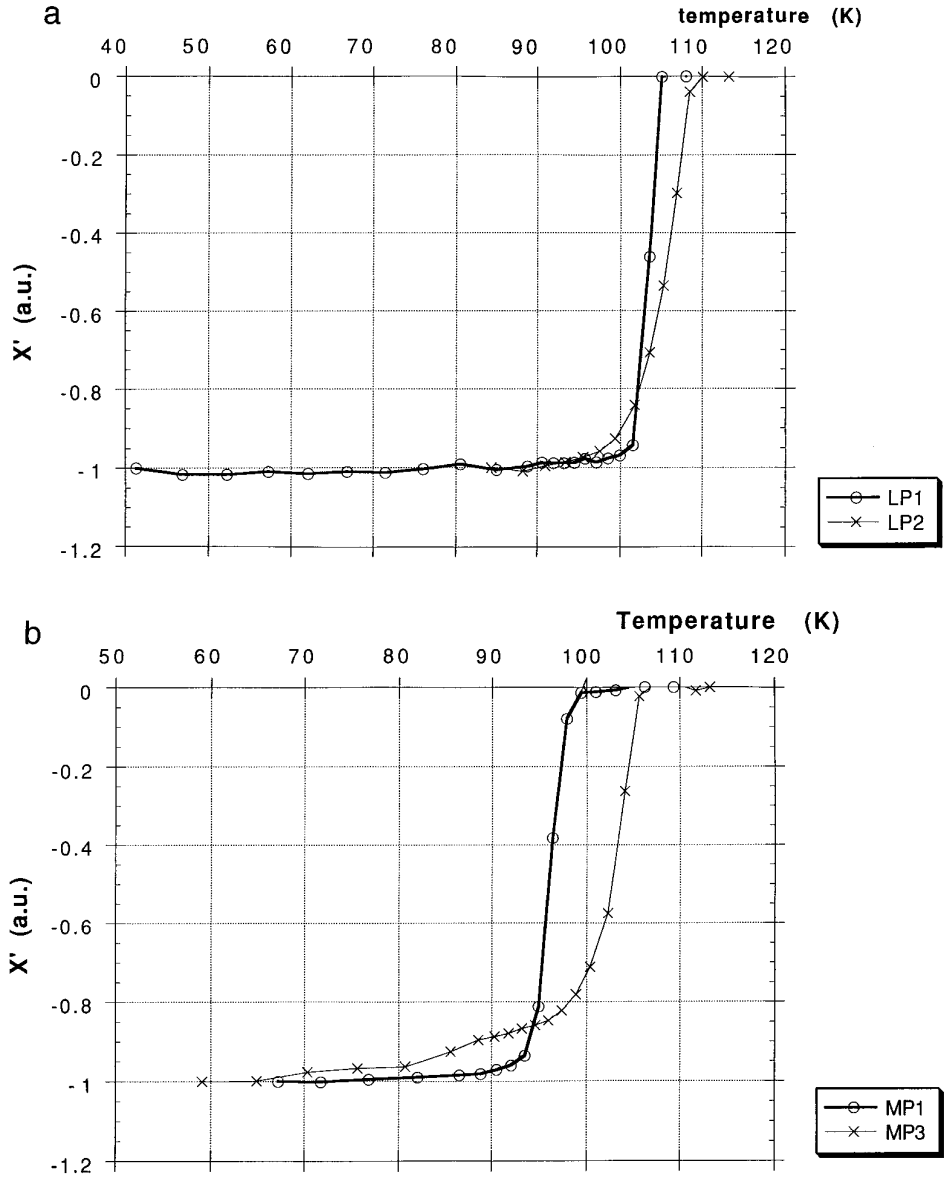

FIG. 2. Thermal variations of the normalized ac magnetic susceptibility for Tl 2212 thin films: (a) as-synthesized under 1 bar O_2 and post-annealed under Ar at 180°C, (b) as-synthesized under 10 bar O_2 and post-annealed under Ar at 180°C, (c) as-synthesized under 70 bar O_2 and post-annealed under Ar at 180°C, and (d) as-synthesized under 10 bar O_2 and post-annealed under Ar at 220°C.

tion of the film. As seen from the T_c's of the films (see Table 2) for low pressure and medium pressure annealings, a good reproducibility of the synthesis can be achieved. Conversely, for high pressure annealings, the synthesis seems to be less reproducible.

All the precursor films exhibited after deposition a 2:2:1:2 Tl:Ba:Ca:Cu stoichiometric composition. After annealing, the thallium content as seen by EDS analysis shifted between 2 and 1.5. At that stage in the process, it is not possible to find a correlation between the thallium content of a film and it's T_c. Measurements made by $^4He^+$ Rutherford backscattering spectroscopy (3) on a high pressure film gave the same average composition, but they also indicated that the film is not completely homogeneous. The thickness measured by the same experiment gave an average value of 0.7 μm. Low and medium pressure oxygen annealed films look quite similar by scanning electron microscopy. Small roughly square grains are visible but the surface appears quite smooth. Small insulating particles are visible on the surface, but less on medium pressure thin films. The TEM observations indicate a very good crystallization with few defects. The nature of the substrate–film interface indi-

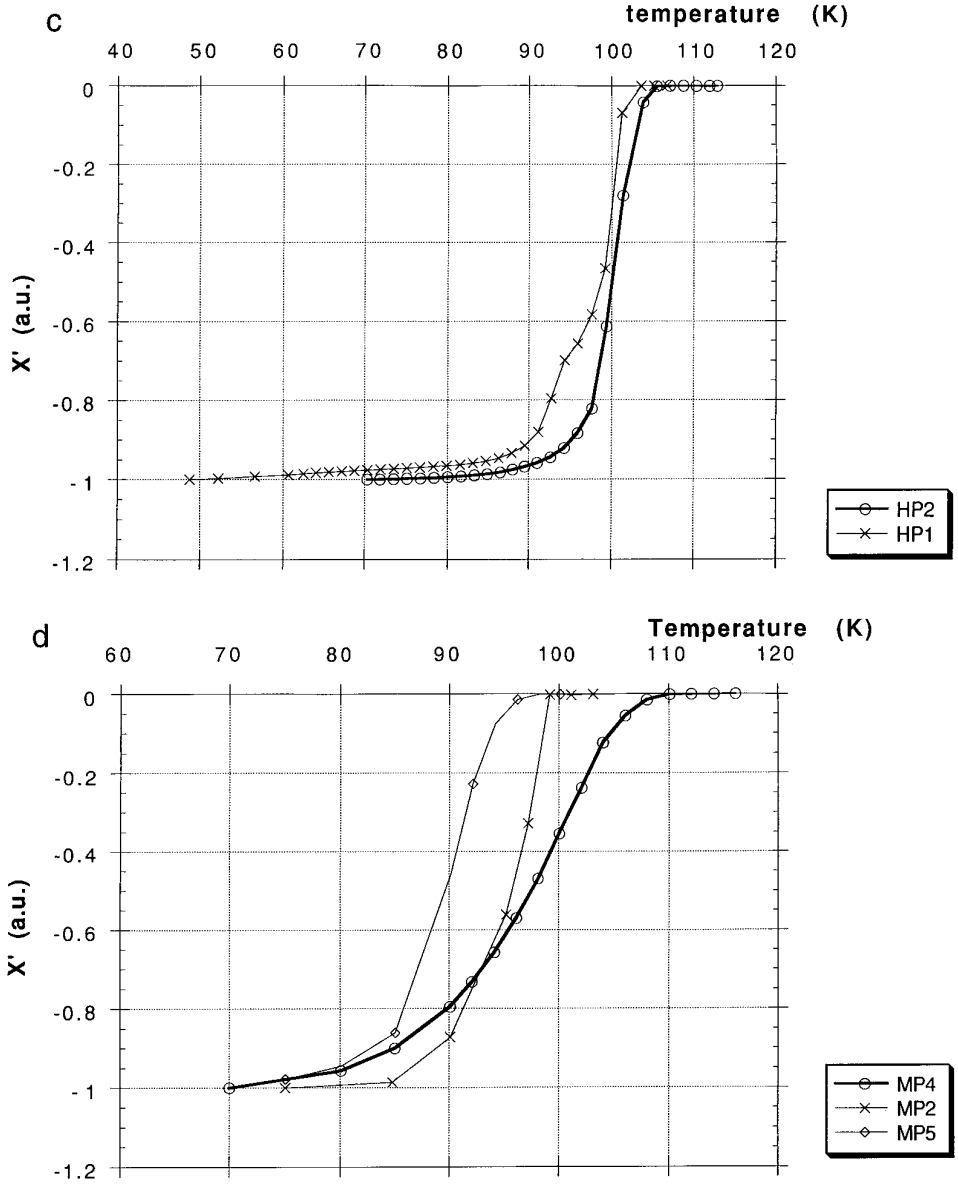

FIG. 2—*Continued*

cates a direct crystallization starting from the substrate. On the surface of high pressure films, there is no visible structure. According to the TEM observations, these high pressure films are highly microcrystalline.

2. XRD Analysis

X-ray diffraction $\theta - 2\theta$ of the films indicates a good crystallization with the *c*-axis perpendicular to the substrate surface (Fig. 1a). The (001) peaks from the Tl 2212 phase and the reflection from the substrate are labeled on the figures. The degree of *c*-axis orientation of the films is measured by XRD rocking curve using the (0 0 12) reflection (Fig. 1b). The full width at half maximum is about 0.8° in good agreement with previous results (12). There is no evidence that the post-annealing treatments modify the crystal structure of the film. Figure 1c shows the XRD scan of the films MP4 and MP5 after post-annealing. The post-annealing treatments of MP4 and MP5 thin films were done at a higher temperature (220°C), thus in more reductive conditions. The XRD scan of these films show no significant change before (Fig. 1a) and after post-annealing (Fig. 1c). Thus one can conclude that the changes in physical properties do not result from a modification of the film crystal structure.

TABLE 2

Low oxygen pressure annealing	T_c as-synthetised	Post-annealing treatment	T_c after post-annealing	n_h
LP1	105 K	none		0.16 ± 0.015
LP2	105 K	10 min 180°C under Ar	108 K	0.14 ± 0.015
Medium oxyen pressure annealing				
MP1	100 K	none		≥0.17 ± 0.015
MP2	99 K	none		0.2 ± 0.015
MP3	99 K	10 min 180°C under Ar	105 K	0.15 ± 0.015
MP4	102 K	5 min 220°C under Ar	106 K	—
MP5	99 K	10 min 220°C under Ar	95 K	0.08 ± 0.02
High oxygen pressure annealing				
HP1	101 K	none		0.2 ± 0.015
HP2	102 K	10 min 180°C under Ar	104 K	0.16 ± 0.015

3. Magnetic Measurements

The T_c measurements have been made by magnetic susceptibility with ac or dc fields of 1 G. As the sample size was unusual, it was not possible to place the films perpendicular to the magnetic field. The observed curves allow only the measurements of T_c and the evaluation of the shape of the transition. In order to compare the various transitions, the superconducting volumes have been normalized to a common value. The figures show both as-synthesized films and post-annealed films for comparison (3).

(*a*) *Low temperature post annealing treatment.* Figures 2a, 2b, and 2c exhibit films which have been post-annealed under argon for 10 min at 180°C.

For LP films (Fig. 2a), after post-annealing, T_c(onset)'s increase but the transition is broadened. There is only 3 K enhancement for LP2 after post-annealing in comparison with LP1. It seems that the film is close to the optimum doping hole density and thus also in oxygen content. The broadening of the transition at T_c is a general trend of the post-annealed samples and can be linked to the inhomogeneity of the oxygen loss during the post-annealing treatment which must induce inhomogeneity of the oxygen stoichiometry and consequently random variation of the hole density throughout the film.

The enhancement for medium pressure films is larger. For instance, MP3 exhibits a T_c increase of 6 K (Table 2). As this film has been annealed under medium oxygen pressure, the oxygen content is larger and thus T_c is decreased since the overdoping is increased. Consequently, with the same post-annealing treatment, it is possible to get a larger enhancement, but not better than the as-synthesized low pressure thin films. With these MP thin films, the superconducting volume starts to decrease after post-annealing which might be induced by the post-annealing treatments as it corresponds to a loss of oxygen and to a degradation of the grain boundaries. With weaker grain boundaries, the magnetic field can penetrate the film more easily thus reducing the measured superconducting volume.

The interpretation of the measurements for the HP thin films is more difficult. For HP1, the transition exhibits two steps. As the sample is highly microcrystalline, the grain boundaries might be more sensitive to the magnetic field than the rest of the film. For HP2, there is only a small T_c variation of 2 K. It appears that it is more difficult to lose oxygen in this case.

(*b*) *High temperature post annealing treatment.* Three films out of the same preparation set were kept to test a post-annealing treatment at a higher temperature. Two films were post annealed at 220°C for 5 (MP4) and 10 (MP5) min under argon. The third film (MP2) was kept as reference.

A T_c enhancement of 4 K for MP4 after 5 min post annealing and a T_c decrease of 5 K for MP5 after 10 min were observed indicating deviation from the optimum of oxygen content or of the doping hole densities for the MP5 thin film. Both MP4 and MP5 transitions exhibit broad transitions characteristic of inhomogeneities in oxygen contents (Fig. 2d). Thus a post-annealing treatment at 220°C induces inhomogeneities in the film oxygen content and, for annealing times as short as 10 min, a too large oxygen loss.

4. XAS Experiments

As shown in previous papers (13), T_c in superconducting copper oxides is primarily sensitive to the doping hole density in the $[CuO_2]_\infty$ or (a, b) planes of these bidimensional structures. To ensure that the XAS spectrum gives information about the whole thin film, one must consider the detection technique used. This problem has been addressed previously by comparing spectra obtained on the

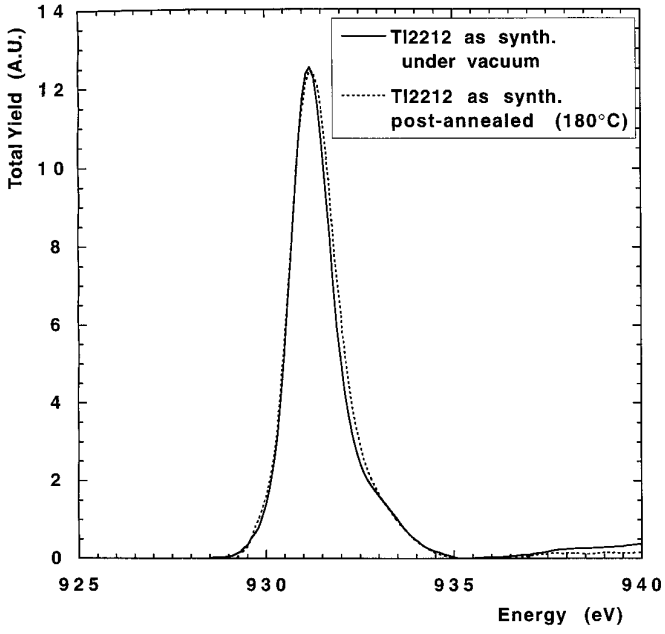

FIG. 3. XAS CuL_3-edges of Tl 2212 thin films as-synthesized under 1 bar O_2 and post-annealed under Ar at 180°C.

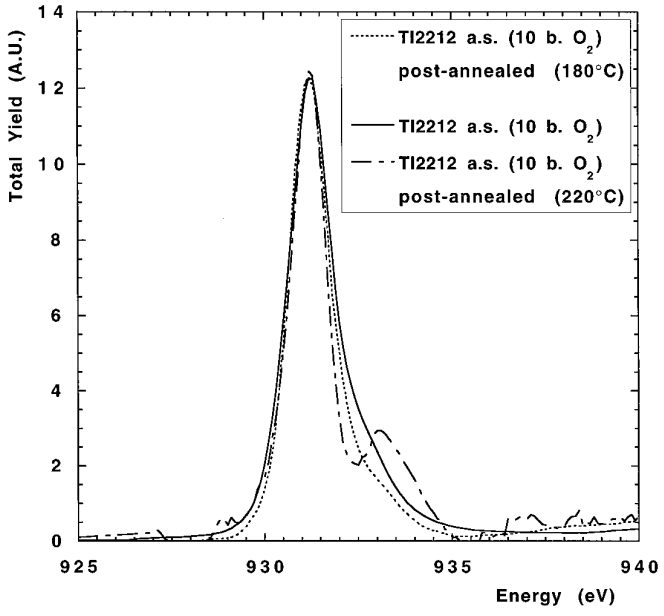

FIG. 4. XAS CuL_3-edges of Tl 2212 thin films as-synthesized under 10 bar O_2 and post-annealed under Ar at 180°C and 220°C.

same samples in total electron yield and fluorescence yield modes since the latter technique is claimed to probe more than 1500 Å under the surface whereas the total yield detection is limited to a maximum layer depth of 150 Å. It has been shown that, after a full correction of the self-absorption in soft X-ray fluorescence which corrects the relative intensities of the $|3d^9\rangle$ and $|3d^9L\rangle$ peaks, the estimated doping hole density calculated from $n_h = I_{|3d^9\rangle}/(_{|3d^9\rangle}+I_{|3d^9L\rangle})$ is very close regardless of the detection technique. To correlate T_c and doping hole density, we will only consider the Cu L_3-edge spectra recorded by the total electron yield method in normal incidence, i.e. with the electric field of the incident wave in the plane of the thin film.

The Cu L_3-edge spectra of the as-synthesized Tl(2212) thin films prepared under vacuum (LP), under 10 bars(MP), and 70 bars(HP) oxygen pressure are shown in Figs. 3, 4, and 5, respectively, alongside the spectra of the corresponding argon annealed samples. In Fig. 4, beside the sample synthesized under 10 bars oxygen are shown the spectra of two thin films post-annealed under argon at 180 and 220°C. The various T_c's, estimated from magnetic susceptibility curves (Fig. 2) and doping hole densities, estimated from a spectral deconvolution in two contributions, are reported in Table 2. These XAS curves were recorded on at least two different sets of each kind of sample (LP, MP, and HP) and the observed relative variations between as-synthesized and post-annealed films were always found.

From these results the following comments can be made:

—As expected, the doping hole density of the as-synthesized film under vacuum (LP1) is smaller than those of the as-synthesized films under medium (MP1-2) and high (HP1) oxygen pressure (Fig. 3). In agreement with the T_c versus n_h curve published previously (7, 13); the T_c of the former thin film is higher than the T_c of the latter suggesting that all the as-synthesized thin films are overdoped.

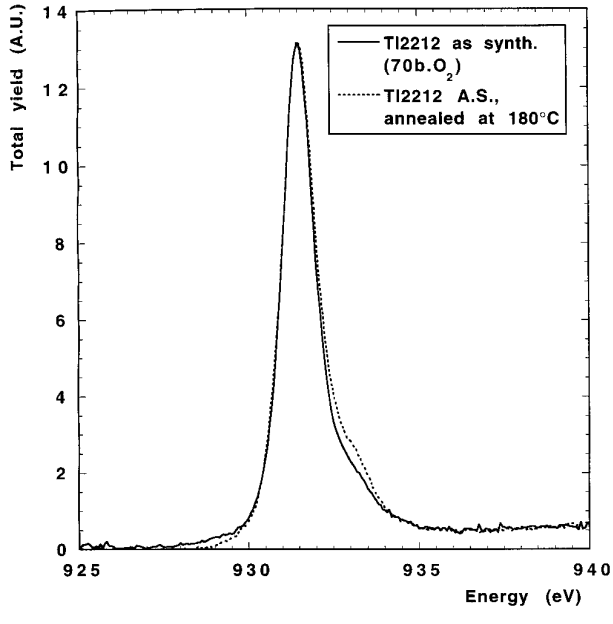

FIG. 5. XAS CuL_3-edges of Tl 2212 thin films as-synthesized under 70 bar O_2 and post-annealed under Ar at 180°C.

—The post-annealed treatment under argon at 180°C results in a decrease in the doping hole density which corresponds to an increase in the T_c. But the T_c of the post-annealed film synthesized under vacuum (LP2) still remains higher than the T_c's of MP3 and HP2 (Table 2). This can be a result of the short post-annealing times (10′) which induces the same oxygen loss in all the samples and consequently the doping hole density in the post-annealed film, synthesized under vacuum, will remain closer to the optimum value than the medium and high pressure ones.

—Raising the post-annealing temperature up to 220°C induces a drastic change in the high energy site of the CuL_3-edge spectrum (Fig. 4). In fact, the observed profile corresponds to the presence of two electronic transitions: the charge transfer transition $|2p^6 3d^9 L\rangle \rightarrow |2p^5 3d^{10} L\rangle$ resulting from doping holes and an extra electronic transition $|2p^6(3d_{z^2}^{10-\varepsilon} 4s^{\varepsilon})\rangle \rightarrow |2p^5(3d_{z^2}^{10} 4s^1)\rangle$, at around 934 eV, resulting from the presence of Cu(I) in its classical dumbbell coordination at the sample surface. The simulation of three peaks thus showed a strong decrease of n_h corresponding to a too large oxygen loss. n_h crosses the optimum value, determined on the T_c versus n_h curve to be 0.12, for 10 min annealing time. Consequently the T_c of this post-annealed thin film (MP5) starts to decrease sharply since it exhibits a T_c of 92 K on the susceptibility curve.

CONCLUSION

In this paper, 2212 thallium cuprate thin films have been thoroughly characterized for the crystallographic, magnetic, and electronic properties through X-ray diffraction, magnetic susceptibility, and polarized X-ray absorption spectroscopy analyses.

The results have been analyzed as a function of the *ex situ* crystallization processes and post-annealing treatments at low temperature under an inert atmosphere. They have confirmed the dependence of T_c's on the doping hole density n_h in the Tl(2212) superconducting thallium copper oxide and the existence of an optimum doping hole value for the best T_c.

The experimental conditions for an optimization of the superconducting properties in such thallium cuprate thin films have been determined, allowing a variation of T_c between 95 and 108 K. They have shown that the optimization process through post-annealing treatments must be thoroughly controlled. They have allowed us to obtain by these treatments an underdoped sample, which is not possible in bulk (7).

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